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(54) RESIN COMPOSITION, ITS CURED ITEM, AND ITS ARTICLE

(57)Abstract:

PROBLEM TO BE SOLVED: To obtain a resin compsn. which is excellent in resistances to heat and thermal shock and is suitable for an optical disk compsn, by compounding an epoxy (meth)acrylate of a urethane (meth)acrylate with a (meth)acrylic ester of trimethylolactane.

SOLUTION: This compsn, contains an epoxy (meth)acrylate or a urethane (meth)acrylate (A), a (meth)acrylic ester of trimethylolactane (B), and optionally a photopolymn. initiator (C) and can be cured with an energy ray such as an X-ray, an electron beam, or ultraviolet rays.

Ingredient C is compounded in the case of curing with ultraviolet rays but not in the case of an X-ray or an electron beam. Pref. the compounding ratio of ingredients A:B:C is 5-85wt.%, 15-95wt.%, 0-30wt.%, the sum being 100wt.%.

AN 1998:36021 CAPLUS
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 ED Entered STN: 22 Jan 1998
 TI Polymer compositions with good hot-water resistance and heat-shock resistance, their cured products, and their articles for optical disks
 IN Tokuda, Kiyohisa; Yoshida, Kenji; Ishii, Kazuhiko; Yokojima, Minoru
 PA Nippon Kayaku Co., Ltd., Japan
 SO Jpn. Kokai Tokkyo Koho, 5 pp.
 CODEN: JKXXAF
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 LA Japanese
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 ICS C08F290-06; C09D004-02; C09D163-10; C09D175-14; C09J004-02; C09J163-10; C09J175-14; G11B007-24
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FAN.CNT 1

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PRAI	JP 1996-184302		19960626		

AB Title compns. comprise (A) epoxy (meth)acrylates or urethane (meth)acrylates and (B) trimethylolactone (meth)acrylates. Cured products of the compns. and articles having layers of the cured products are also claimed. Thus, a composition comprising Kayarad UX 6101 (urethane acrylate) 30, trimethylolactone triacrylate 70, and Irgacure 184 3 parts was applied on a Ni plate, covered with a silane-treated glass plate, and irradiated with a high-pressure Hg lamp to give a sample showing good hot-water resistance, good heat-shock resistances, and hardness 80.

ST heat resistance acrylic polymer prep; water resistance acrylic polymer prep

IT Polyurethanes, preparation
 RL: DEV (Device component use); IMF (Industrial manufacture); PRP (Properties); PREP (Preparation); USES (Uses)
 (acrylic; polymer compns. with good hot-water and heat-shock resistances and hardness, their cured products, and their articles for coatings for optical disks)

IT Coating materials
 Heat-resistant materials
 Optical disks
 Water-resistant materials
 (polymer compns. with good hot-water and heat-shock resistances and hardness, their cured products, and their articles for coatings for optical disks)

IT 202602-72-0P 202667-37-6P 202667-38-7P
 RL: DEV (Device component use); IMF (Industrial manufacture); PRP (Properties); PREP (Preparation); USES (Uses)
 (polymer compns. with good hot-water and heat-shock resistances and hardness, their cured products, and their articles for coatings for optical disks)

DERWENT-ACC-NO: 1998-126195

DERWENT-WEEK: 199812

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TITLE: Resin composition contains an epoxy (meth)acrylate or urethane (meth)acrylate and a (meth)acrylate of tri:methylol:octane

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PATENT-ASSIGNEE: NIPPON KAYAKU KK[NIPK]

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ABSTRACTED-PUB-NO: JP 10007751 A

BASIC-ABSTRACT:

A resin composition contains: (A) an epoxy (meth)acrylate or urethane (meth)acrylate; and (B) a (meth)acrylate of trimethylol octane.

USE - The resin composition is used for channel materials for photodisc recording media, overcoating agents, hard coating agents for photo-discs. Articles, particularly photo-discs having layers formed from cured products of the resin composition are claimed. The resin composition is also useful for printing inks, paints, adhesives, insulating paints and gloss varnishes.

ADVANTAGE - The composition cures rapidly under irradiation with UV and has good hot water resistance, heat shock resistance and transparency. The cured product has high hardness.

TITLE-TERMS: RESIN COMPOSITION CONTAIN EPOXY METHO ACRYLATE URETHANE TRI METHYLOL OCTANE

ADDL-INDEXING-TERMS:

ACRYLATE! METHACRYLATE!

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention]This invention relates to the suitable energy-line hardenability resin composition for optical discs which record and play a resin composition, especially a lightwave signal at high speed and with high density, such as a groove material for optical disk recording media, an overcoat agent, and adhesives, its hardened material, and an article.

[0002]

[Description of the Prior Art]Now, polycarbonate resin and methyl methacrylate resin are used as a material of a noncommercial optical disc. The material of the optical disc which consists of monomers, such as 2,2-bis(4-(meth)acryloyloxy phenyl)propane and styrene, is also proposed. As an industrial optical disc, development of the disk which used inorganic glass as the substrate for quality requirements, such as long term reliability, is also performed, and development of the groove material for glass base materials is also furthered simultaneously.

[0003]

[Problem(s) to be Solved by the Invention]The quality the industrial optical disc excelled [quality] in hot water resistance, heat shock-proof nature, high hardness, transparency, etc. as the characteristic to a groove material since long term reliability was required is demanded. Although many constituents are conventionally known as an ultraviolet curing type resin composition, the actual condition is that the constituent which fully fills the above-mentioned characteristic is not found out till today. The photo-curing type adhesive composition for optical discs which used glass as the substrate is proposed by JP,59-71317,A. In order to use mono-(meta) acrylate with an OH radical as the main ingredients and to use it as a groove material into molecules, such as 2-ethyl-2-hydroxyethyl (meta) acrylate, this constituent has hot water resistance, insufficient hardness, etc., and is unsuitable.

[0004]

[Means for Solving the Problem] In order to solve the above-mentioned problem, this invention persons succeeded in providing a resin composition suitable for especially a constituent for optical discs and its hardened material in which hardening was quick and hot water resistance, heat shock-proof nature, and hardness were excellent by ultraviolet rays wholeheartedly as a result of research. Namely, a resin composition, wherein this invention contains acrylic ester (meta) (B) of (1) epoxy (meta) acrylate or urethane (meta) acrylate (A), and TORIMECHI roll octane, (2) An article which has a layer which consists of a hardened material of a resin composition of a hardened material of a resin composition of a resin composition of (1) containing a photopolymerization initiator (C), (3), (1), or (2), (4), (1), or (2), and (5) articles are related, without an article of (4) which is an optical disc.

[0005] In a resin composition of this invention, acrylic ester (meta) (B) of epoxy (meta) acrylate or urethane (meta) acrylate (A), and TORIMECHI roll octane is contained as an essential ingredient, and a photopolymerization initiator (C) is contained as an optional component. Epoxy (meta) acrylate and urethane (meta) acrylate may be used alone, and may be used together. A resin composition of this invention is a resin composition of energy-line hardenability. As an energy line, X-rays, an electron beam, ultraviolet rays, etc. are raised, for example. When using a resin composition of this invention as a resin composition of ultraviolet curing nature, a photopolymerization initiator (C) is used. When making it harden with X-rays or an electron beam, the photopolymerization initiator (C) does not need to use it.

[0006] Epoxy (meta) acrylate used for a resin composition of this invention is a reactant of an epoxy resin and acrylic acid (meta). As an epoxy resin used here, for example A bisphenol A type epoxy resin, Bisphenol F type epoxy resin, biphenyl diglycidyl ether, Phenol novolak type epoxy resin, cresol novolak type epoxy resin, a trisphenol methane type epoxy resin, aliphatic series or an epoxidation thing of an alicycle-like olefin, epoxidation polybutadiene, epoxidation rosin, etc. are raised.

[0007] As urethane (meta) acrylate used for a resin composition of this invention, a polyol compound (a) and a reactant of organic polyisocyanate (b) and hydroxyl group content (meta) acrylate (c) are raised, for example. As a polyol compound (a), for example Ethylene glycol, propylene glycol, Neopentyl glycol, 1,6-hexanediol, 3-methyl-1,5-pentanediol, 1,9-nonanediol, 1,4-butanediol, a diethylene glycol, Tripropylene glycol, 1,4-dimethylolbenzene, 1,4-dimethylolcyclohexane, Bisphenol A polyethoxydiol, a polypropylene glycol, Diol, these diol, succinic acid, such as polytetramethylene glycol, Maleic acid, itaconic acid, phthalic acid, isophthalic acid, terephthalic acid, The polyester polyol which are a reactant of dibasic acid, such as adipic acid and dimer acid, or these acid anhydrides. The polycaprolactone polyols and polycarbonate polyols etc. which are reactants with said diol, said dibasic acid or these acid anhydrides, and epsilon-caprolactone can be mentioned. As organic polyisocyanate (b), for example Tolylene diisocyanate, Isophorone diisocyanate, xylylene diisocyanate,

diphenylmethane-4,4'-diisocyanate, Dicyclopentaniol diisocyanate, hexamethylene diisocyanate, 2 and 4, 4'-trimethyl hexamethylene diisocyanate, 2, 2', 4-trimethyl hexamethylene diisocyanate, etc. can be mentioned.

[0008]As hydroxyl group content (meta) acrylate (c), For example, 2-hydroxyethyl (meta) acrylate, 2-hydroxypropyl (meta) acrylate, A reactant of 1,4-butanediol mono- (meta) acrylate, 2-hydroxyethyl (meta) acrylate, and epsilon-caprolactone, 2-hydroxy-3-phenyloxy propyl (meta) acrylate, penta ERIS RITORUTORI (meta) acrylate, GURISERINJI (meta) acrylate, etc. can be mentioned.

[0009]This urethane (meta) acrylate can be obtained by making hydroxyl group content (meta) acrylate (c) react, after making organic polyisocyanate (b) react to a polyol compound (a) for example. It is desirable especially preferred to make 1.1-2.5 Eq of isocyanate groups of organic polyisocyanate (b) react to 1 Eq of hydroxyl groups of polyesterdiol (a), and a reaction of polyesterdiol (a) and organic polyisocyanate (b) is 1.3-2.0 Eq. 70-100 °C of reaction temperature is preferred, and reaction time of about 5 to 20 hours is preferred. Next, hydroxyl group content (meta) acrylate (c) is made to react to polyesterdiol (a) and reactant (l) with organic polyisocyanate (b). It is 1.0-1.1 Eq to react 0.95-1.5 Eq of hydroxyl groups of hydroxyl group content (meta) acrylate (c) to 1 Eq of isocyanate groups of reactant (l) desirable especially preferably. 60-100 °C of reaction temperature is preferred, and reaction time is 5 to 20 hours. During a reaction, in order to prevent a polymerization, polymerization inhibitor (for example, p-methoxy phenol, methylhydroquinone, etc.) and reaction catalysts (for example, di-n-butyl tin etc.) for promoting a reaction can also be used.

[0010]Acrylic ester (B) used for this invention (meta), By a publicly known method, it can obtain by making acrylic acid (meta) react to TORIMECHI roll octane at temperature of 70-130 °C preferably under existence of polymerization inhibitor, such as an esterification catalyst of p-toluenesulfonic acid or sulfuric acid and hydroquinone, for example. As desirable (meta) acrylic ester (B), for example, TORIMECHIRORUOKUTANTORI acrylate is mentioned especially.

[0011]In this invention, a photopolymerization initiator (C) is used as an optional component. As an example of a photopolymerization initiator (C), for example 2-hydroxy-2-methyl-1-phenylpropan-1-one, 1-hydroxycyclohexyl ketone, methylphenylglyoxylate, Benzyl dimethyl ketal, MIHIRAZU ketone, 2-benzyl-2-dimethylamino 1-(4-morpholinophenyl)- The butanone- 1, 2-chloro thioxan ton, 2,4-diethylthio xanthone, 2-isopropyl thioxan ton, Benzoyl ethyl ether, benzoin iso-propyl ether, o-benzoylbenzoic acid methyl ester, p-dimethylamino acetophenone, 2,4,6-trimethyl benzoyl diphenylphosphine oxide, Bis(2,6-dimethoxybenzoyl)-2,4,4-trimethyl pentyl phosphine oxide, 2-ethylantraquinone, 2-KURORU anthraquinone, benzophenone, p-dimethylamino benzophenone, 2-methyl- 1 - [4-(methylthio) phenyl] -2-morpho no propan-1-one etc. are mentioned. This photopolymerization initiator (C) can mix and use a kind or two sorts or more.

[0012]The amount of epoxy (meta) acrylate used by this invention, or urethane (meta) acrylate (A) used, As opposed to a total amount of the (A) ingredient and the (B) ingredient which are used by this invention, and the (C) ingredient, It is 10 to 50 % of the weight still more preferably ten to 80% of the weight more preferably five to 85% of the weight, (Meta) Preferably the amount of acrylic ester (B) used 15 to 95 % of the weight, It is 25 to 80 % of the weight still more preferably, and the amount of photopolymerization initiator (c) used is 1 to 15 % of the weight still more preferably one to 20% of the weight zero to 30% of the weight 20 to 90% of the weight more preferably. When using together epoxy (meta) acrylate and urethane (meta) acrylate as a (A) ingredient, both are used at an arbitrary rate and used in the use range of the above-mentioned (A) ingredient as both total amount.

[0013]It is made [using unsaturation group content compounds (d) other than (A) and the (B) ingredient, or] to a resin composition of this invention. As an unsaturation group content compound (d), for example 2-hydroxyethyl (meta) acrylate, 2-hydroxypropyl (meta) acrylate, 1,4-butanediol mono- (meta) acrylate, 2-ethylhexyl polyoxy (meta) acrylate, benzyl (meta) acrylate, Phenyloxy ethyl (meta) acrylate, phenyloxy ethyloxy ethyl (meta) acrylate, Tricyclodecane mono- (meta) acrylate, isobornyl (meta) acrylate, Acryloyl morpholine, N-vinylcaprolactam, 2-hydroxy-3-phenyloxy propyl (meta) acrylate, Tricyclodecane JIMECHIRORUJI (meta) acrylate, TORIMECHI roll pro pantry (meta) acrylate, Trimethylolpropane TORIPUPOKISHITORI (meta) acrylate, GURISE lint repro POKISHITORI (meta) acrylate, hydroxy pivalate neopentyl glycol di(metha)acrylate, Bisphenol A poly ETOKISHIJI (meta) acrylate, penta ERIS RITORUTORI or tetra (meta) acrylate, dipentaerythritol penta, and hexa (meta) acrylate, Ditrithymol propane tetra (meta) acrylate, polyester (meta) acrylate, etc. can be mentioned. The amount of unsaturation group content compound (d) used is 0 to 40 % of the weight still more preferably zero to 60% of the weight more preferably zero to 80% of the weight among a resin composition of this invention.

[0014]In a resin composition of this invention, if needed further A photopolymerization start auxiliary agent, nonresponsive resin. for example, petroleum resin, a polyester elastomer, and a polyurethane elastomer. Color pigments, such as acrylic polymer and isobutylene isoprene rubber, polymerization inhibitor, a good SO agent, a bulking agent, an antioxidant, light stabilizer, an ultraviolet ray absorbent, an organic solvent, a defoaming agent, a leveling agent, a coupling agent, and other auxiliary agents can be used together. As a photopolymerization start auxiliary agent, amines, such as 2-dimethylaminoethyl benzoate, a dimethylamino acetophenone, p-dimethylamino ethyl benzoate, p-dimethylamino isoamyl benzoate, and p-dimethylamino benzoaldehyde, are raised, for example. The amount of photopolymerization start auxiliary agent used is usually about 0 to 10 % of the weight still more preferably zero to 15% of the weight preferably in a resin composition.

[0015]The resin composition of this invention can prepare each of above-mentioned

ingredients by carrying out heating and dissolving, or mixing and distribution.

[0016]Hardening of a resin composition of this invention can be performed with a conventional method by irradiating with an energy line. What is necessary is just to irradiate with ultraviolet rays, for example using low pressure or a high-pressure mercury-vapor lamp, a metal halide lamp, a xenon lamp, etc., when using ultraviolet rays as an energy line. What is necessary is just to irradiate with X-rays or an electron beam, for example using an X-ray irradiation device or an electron beam irradiation device, when using X-rays and an electron beam as an energy line.

[0017]Although especially a resin composition of this invention is useful as objects for optical discs, such as an overcoat agent as a groove material for optical discs (resin composition for making a slot form on an inorganic glass board) used as an inorganic glass board, and a protective film of record film of an optical disc, and a hard court agent of an optical disc, For other uses, it is useful to printer's ink, a paint, gloss varnish, adhesives, resist, etc. When using for an optical disc, a resin composition of this invention can also be said to be a resin composition for optical discs.

[0018]If an article of this invention has a layer (only henceforth a hardening layer) which consists of a hardened material of a resin composition of above-mentioned this invention, there will be no restriction in particular, for example, an optical disc, an optical card, an IC card, an ID card, etc. will be raised. As an optical disc, an optical disc, DVD (digital versatile or video disk), etc. to which reading of an optical disc only for reading of CD (compact disk), LD (laser disc), etc., MO (magneto-optical disc), etc. and writing are made, for example are raised.

[0019]What is necessary is just to perform it as follows, for example, if an optical disc is made into an example and a process of an article which has a hardening layer of a resin composition of this invention is described. Formation of a slot on a glass substrate using a resin composition for optical discs of this invention, A resin composition for optical discs is applied with a spin coat method etc. on La Stampa (metallic mold), A slot is formed on a glass substrate by carrying so that air may not go a glass substrate into a spreading side, pushing in a glass substrate, irradiating with ultraviolet rays, hardening a groove material, and making following **** La Stampa release from mold from a glass substrate. As for the thickness, when applying a groove material on La Stampa, it is preferred to usually be referred to as about 10-100micro. Thus, metal (for example, alloys, such as Gd, Tb, Te, germanium, Au, Pt, Pb, Sb, Ti, Ag, Se, TeO₂, and Fe) is made to vapor-deposit with a conventional method, and record film is made to form on a substrate with which a slot obtained was formed. A resin composition for optical discs (overcoat agent for optical discs) is preferably applied to thickness of two to 7 micro on a sputtering film (record film) with a spin coat method etc. after that, and an overcoat film (protective film) is formed by irradiating with ultraviolet rays and hardening an overcoat agent. In these methods, hardening of a resin composition can also be based on electron

beam irradiation instead of UV irradiation.

[0020]

[Example] Hereafter, an example explains this invention still more concretely. The part in an example is a weight section.

According to the combination presentation of the Examples 1-3 and comparative example 1 table 1, this invention or the resin composition (resin composition for optical discs) of the comparative example was prepared. Subsequently, isopropyl alcohol containing 1 % of the weight of alpha-methacryloxy propyl trimethoxysilane was applied to the pure soda glass substrate, it heated for 30 minutes at 100 **, and baking finish of this Silang was performed. Thus, the prepared resin composition was applied by the spin coater on the nickel board, it carried so that air bubbles might not go a silanizing glass plate into a spreading side, and it glared from the glass surface with the high-pressure mercury-vapor lamp (the Japan Storage Battery Co., Ltd. make, 2 kW), and this constituent was stiffened. It examined about a water resisting property, heat shock-proof nature, and hardness using this.

(Appraisal method)

Water resisting property: After dipping the obtained substrate in 100 ** hot water for 1 hour, the existence of the abnormalities of the hardening layer on a substrate was observed.

O It is completely normal.

x A white blush mark, HAKURI, etc. have occurred.

Heat-shock [-proof] nature: After dipping the obtained substrate for 5 minutes into liquid nitrogen, the existence of the abnormalities of a substrate was observed.

O It is completely normal.

x A crack, HAKURI, etc. have occurred.

Hardness: This constituent was applied by a thickness of 2 mm on the nickel board, it hardened in N₂ gas with the high-pressure mercury-vapor lamp, and this hardness was measured with the Shore D hardening plan.

[0021]

[Table 1]

Table 1 EXAMPLE Comparative example 1 2 3 1 KAYARAD. R-114 *1 15 15 KAYARAD. UX-6101*2 30 15 30 TORIMECHIRORUOKUTANTORI acrylate 70 55 50 KAYARAD R-604*3 30 tetrahydrofurfuryl acrylate 10 trimethylolpropane triacrylate . 10 70 IRGACURE 184*4 3 3 3 3 --
----- water resisting property O O O x Heat shock-proof nature O O O x
Hardness 80 90 85 85 [0022] notes *1 KAYARAD R-114: Nippon Kayaku Co., Ltd. make and a bisphenol A type epoxy resin (the product made from Oil recovery Shell Epoxy.) Epoxy acrylate *2 KAYARAD UX-6101 which is a reactant of Epicoat 828 and acrylic acid : The Nippon Kayaku Co., Ltd. make, Urethane acrylate *3 KAYARAD R-604 : The Nippon Kayaku Co., Ltd. make, 5-ethyl-2-(2-hydroxy-1,1-dimethylethyl)-5-(hydroxymethyl)-1,3-dioxane

diacrylate *4 IRGACURE 184: The Ciba-Geigy make, 1-hydroxycyclohexylphenyl ketone, a photopolymerization initiator [0023]The resin composition of this invention is excellent in a water resisting property and heat shock-proof nature, and its hardness is also good so that clearly from the evaluation result of Table 1.

[0024]

[Effect of the Invention]It is hard, and the hardness of the hardened material produced by hardening this is excellent in hot water resistance, heat shock-proof nature, and transparency, and the resin composition of this invention has it to the groove material for optical discs, the overcoat agent for optical discs, especially the hard court agent for optical discs, etc. [useful]

[Translation done.]

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CLAIMS

[Claim(s)]

[Claim 1]Epoxy (meta) acrylate or urethane (meta) acrylate (A), and a resin composition containing acrylic ester (meta) (B) of TORIMECHI roll octane.

[Claim 2]A resin composition of claim 1 containing a photopolymerization initiator (C).

[Claim 3]A hardened material of the resin composition according to claim 1 or 2.

[Claim 4]An article which has a layer which consists of a hardened material of the resin composition according to claim 1 or 2.

[Claim 5]An article of claim 4 whose article is an optical disc.

[Translation done.]